a monocarboxylic acid at an alkaline pH to generate acetaldehyde in situ and then cross-linking said cereal starch until its alkaline fluidity is between 60 cc. and 90 cc. with the acetaldehyde generated during the acylation step by lowering the pH of the reaction mixture below 4.

In a fourth aspect this invention is a process of preparing a cross-linked cereal starch acylate of a monocarboxylic acid, which comprises acylating said cereal starch with a vinyl ester of a monocarboxylic acid or an anhydride and then reacting said starch with a cross-linking agent until said starch has an alkaline fluidity of from 50 cc. to 90 cc.

We have attained the foregoing objects by preparing certain cross-linked starch acylates. These cross-linked starch acylates are prepared by reacting granular starch with a monofunctional acylating agent and a polyfunctional cross-linking agent. However, not all cross-linked starch acylates have the paste properties necessary for use in fruit pie starches. The cross-linked cereal starch acylates of this invention have an alkaline fluidity of from about 50 cc. to 90 cc. Inasmuch as the test used to measure the alkaline fluidity of the cross-linked starch acylates is described in some detail below, it is sufficient for the purpose of understanding this invention to realize at this point that the alkaline fluidity of the cross-linked starch acylate is a measurement of the viscosity of the cross-linked starch having essentially no monofunctional acylate groups. In other words, the alkaline fluidity is purely a measurement of the viscosity of the cross-linked starch. The monoacylate groups are apparently saponified during the alkaline fluidity test. If the alkaline fluidity of the cross-linked cereal starch is below 50 cc., the baked pie filling is watery and runs. In effect, the starch granule has not been toughened sufficiently to resist the acid pH. On the other hand, if the alkaline fluidity of the cross-linked cereal starch is above 90 cc., the starch is inhibited to such an extent that the fruit settles out of the pie filling prior to baking. In both cases, the starch paste is unsatisfactory since it fails to give the pie filling the necessary body.

The acyl groups of the cross-linked cereal starch acylates not only give the pie starch improved clarity, texture and freeze-thaw resistance, but also lower the pasting temperature of the starch. In the absence of these acyl groups, cross-linked cereal starches having an alkaline fluidity of from 50 cc. to 90 cc. may be too inhibited to paste properly. Accordingly, the pie filling lacks the necessary machine depositing characteristics and the baked pie is watery. In effect the acyl groups give the pie starch the high initial viscosity, which is necessary in machine depositing, while the cross-linking agents toughen up the granule. Accordingly, the cross-linking step and acylation step are both necessary in order to get a pie starch having the necessary paste characteristics.

The alkaline fluidity test is a convenient method for controlling the extent to which a starch is being cross-linked. However, cereal starch often varies in its paste properties depending, for example, on the time the cereal grain is harvested, and this affects the properties of the starch derivatives made from it. Because of this variability in the parent starch, some cross-linked starch acylates falling within the prescribed alkaline fluidity range may be too inhibited or not toughened sufficiently for use in fruit pie fillings. While the alkaline fluidity test is a means for arriving at a desirable product, the final product should, for fruit pie use, have a paste viscosity at pH 3.5 of at least 700 gm.-cm. after 15 minutes and of at least 600 gm.-cm. after 40 minutes at 201° F., as measured on a Corn Industries Research Foundation viscometer. (The details of this test, referred to as the "CIV test," are described below). Preferably the cross-linked starch acylates should have a 15 minute paste viscosity of at least 740 gm.-cm. and a 40 minute paste viscosity of at least 680 gm.-cm. If the cross-linked starch acylate has a 15 minute paste viscosity of less than 700 gm.-cm. it is too inhibited for use in fruit pies, while if the 15 minute paste viscosity is more than 700 gm.-cm. but the 40 minute paste viscosity is less than 600 gm.-cm., the starch granule has not been toughened sufficiently. However, normally the alkaline fluidity standard is sufficient to determine when the desired product has been obtained even though it is not the sole criterion.

Those products, which are not sufficiently toughened (i.e. the 40 minute CIV at 201° F. is less than 600 gm.-cm.) can be used advantageously for cream pie fillings while those products which are inhibited (i.e. the 15 minute CIV at 201° F. is less than 700 gm.-cm.) can be used as thickeners for alkaline printing inks.

The preferred starches of this invention are the unmodified common-variety cereal starches, such as corn starch, wheat starch, rye starch, rice starch, etc. Various modified starches may also be used in this invention. However, modified starches, such as those which have been oxidized according to United States Patent 2,108,862 to Kerr, have a lower viscosity after cross-linking and acylation than the unmodified cross-linked cereal starch acylates. This is particularly surprising since the modified starches of Kerr prior to acylation and cross-linking have a higher viscosity than the unmodified native starch.

The polyfunctional cross-linking agents of this invention are etherifying agents and esterifying agents having at least two functional groups that react with hydroxyl groups of the starch. The term "polyfunctional cross-linking agent" refers to compounds having at least two groups capable of reacting with the hydroxyl groups of starch, such as, aldehyde groups, ethylenically unsaturated groups, epoxy groups, halo groups, keto groups, etc. Starches cross-linked with monofunctional cross-linking agents, such as acetaldehyde, are subject to partial hydrolysis when cooked for extended periods at an acid pH. The following are representative of the polyfunctional cross-linking agents, which can be used in this invention: ethylenically unsaturated aldehydes, such as acrolein and crotonaldehyde; dihaloalkanes, such as ethylene dichloride, 1,2-propylene dibromide, 2,6-hexylene dichloride; dialdehydes, such as glyoxal and adipaldehyde; methylol compounds, such as dimethylol urea; epihaloalkanes, such as epichlorohydrins, 1,2-epoxy-4-chlorobutane and 1,2-epoxy-5-bromopentane; polybasic acid halides, such as phosphorous oxychloride and adipyl chloride; etc. These etherifying and esterifying agents can be used in an amount equal to from about 0.01% to 10% by weight of dry starch. Although the amount of cross-linking reagent added to the starch is not particularly critical so long as the product has the proper alkaline fluidity, it is economically desirable to use as low a concentration of cross-linking reagent as possible. Furthermore, it is important that the reaction of the cross-linking agent with starch be capable of easy control. It is still more important that the cross-linked starch acylate have a relatively constant viscosity during the cooking of the starch under acid conditions. Phosphorous oxychloride, acrolein and epichlorohydrin are our preferred cross-linking agents, which fulfill all of the above requirements. For example, acrolein is preferably used in a concentration of 0.10% to 0.30% by weight of the dry starch, epichlorohydrin is preferably used in a concentration of from 0.01% to 0.30% and phosphorous oxychloride is preferably used in a concentration of from 0.01% to 0.30%. It is rarely economically advisable to use more than 1% by weight of these cross-linking agents. Furthermore, the more cross-linking agent used, the harder it is to control the extent of cross-linking. The reaction of the phosphorous oxychloride and epichlorohydrin can be terminated or essentially curtailed by adjusting the pH of the alkaline reaction mixture, while the acrolein reaction can be terminated by adding sodium bisulfite to the reaction mixture. It must be emphasized